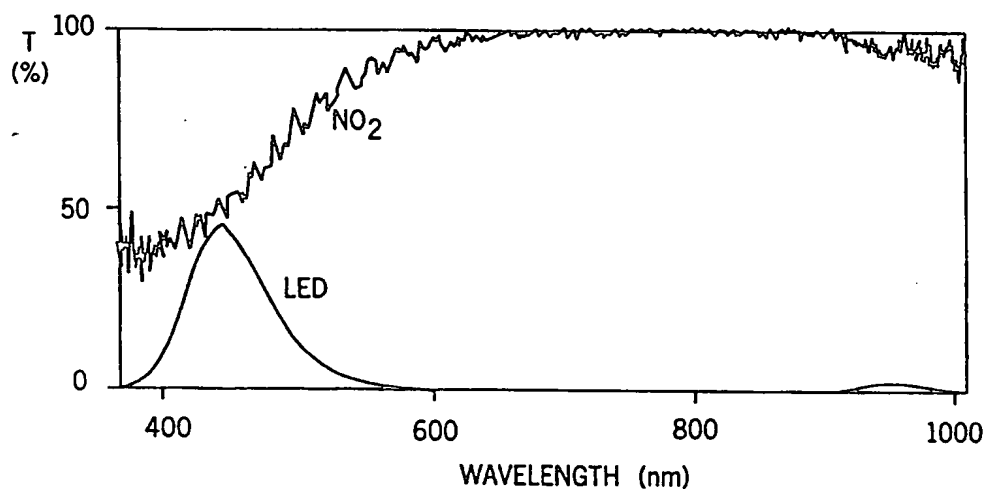




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>G01N 21/31, G01J 3/10</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 99/53297</b> <b>(43) International Publication Date:</b> 21 October 1999 (21.10.99)
<b>(21) International Application Number:</b> PCT/IB99/00645 <b>(22) International Filing Date:</b> 12 April 1999 (12.04.99)  <b>(30) Priority Data:</b> 09/059,805                      14 April 1998 (14.04.98)                      US  <b>(71) Applicant:</b> INSTRUMENTARIUM CORPORATION [FI/FI]; Teollisuuskatu 27, FIN-00510 Helsinki (FI).  <b>(72) Inventor:</b> WECKSTRÖM, Kurt, P.; Teollisuuskatu 27, FIN-00510 Helsinki (FI).  <b>(74) Agent:</b> FETTERLEY, Daniel, D.; Andrus, Sceales, Starke & Sawall, LLP, Suite 1100, 100 East Wisconsin Avenue, Milwaukee, WI 53202 (US).		<b>(81) Designated States:</b> CA, JP, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE).  <b>Published</b> <i>With international search report.</i>

**(54) Title:** SENSOR ASSEMBLY AND METHOD FOR MEASURING NITROGEN DIOXIDE



**(57) Abstract**

A sensing apparatus and method for use in the optical absorption analysis of the NO<sub>2</sub> content of a gas sample. The apparatus and method employ radiation from a semiconductor radiation source. The emission spectrum of the radiation has a maximum wavelength of about 600 nm, preferably 380 – 520 nm. The radiation is passed through the gas sample and sensed by a detector to provide an output signal indicative of the NO<sub>2</sub> content of the gas sample. The sensor apparatus and method may be employed in conjunction with other gas sensing apparatus and methods, such as IR CO<sub>2</sub> measurement or NO sensing.

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakhstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

SENSOR ASSEMBLY AND METHOD  
FOR MEASURING NITROGEN DIOXIDE

BACKGROUND OF THE INVENTION

5           The present invention relates to a sensor assembly and method used for analysis of nitrogen dioxide. The sensor assembly includes a light emitting diode as radiation source, a sample chamber containing the gas to be measured, and at least one radiation detector located to receive the radiation emitted  
10 by the radiation source and passed through the gas to be measured. The invention also relates to the analysis of gases containing nitrogen dioxide or nitric oxide.

          The analysis of small concentrations of nitrogen dioxide ( $\text{NO}_2$ ) is typically measured using a sensor for nitric  
15 oxide ( $\text{NO}$ ) based on chemiluminescence. The procedure is first to measure the background concentration of  $\text{NO}$  and then to convert all  $\text{NO}_2$  to  $\text{NO}$  in an oven and after that remeasure the  $\text{NO}$  content. The difference between the two readings gives an estimation of the concentration of nitrogen dioxide. The method is sensitive  
20 to below ppm levels but the measurement cannot be performed reliably in real time especially if the  $\text{NO}$  background level changes. This is the case when measuring  $\text{NO}$  delivered to a patient or when measuring the endogenic  $\text{NO}$  concentration produced in a patient.

25           Nitrogen dioxide is a highly toxic gas often produced from  $\text{NO}$  in the presence of oxygen. As a precaution, it has therefore been proposed to monitor inhaled  $\text{NO}_2$  concentrations to prevent damage to the patient. It is advisable to measure the  $\text{NO}_2$  concentration on a breath-to-breath basis, meaning that a  
30 response time of about 200 ms is required. This is difficult to meet using a  $\text{NO}_2$  to  $\text{NO}$  converter.

          The same applies for the commonly used electrochemical sensor. It is small and relatively cheap but the response time is too long and the sensitivity low. Such a cell also has a  
35 limited lifetime and other gases may interfere with the desired gas measurement. Infrared absorption could also be used to measure  $\text{NO}_2$  but the sensitivity is low unless the measuring chamber is very long. A long chamber means increased volume and increased response time. Therefore, this method cannot be used  
40 clinically. A good review of all mentioned measuring methods is

found in S.C. Body et al.: Nitric oxide: Delivery, Measurement, and Clinical Application (Journal of Cardiothoracic and Vascular Anaesthesia, Vol. 9, No. 6, 1995: pages 748-763).

It is well known that nitrogen dioxide is one of the few gases that absorbs light in the visible region, see e.g. the reference T.C. Hall, Jr. and F.E. Blacet: Separation of the Absorption Spectra of  $\text{NO}_2$  and  $\text{N}_2\text{O}_4$  in the Range of 2400 - 5000 Å (The Journal of Chemical Physics, Vol. 20, No. 11, 1952: pages 1745-1749). To the eye the gas looks brownish in low concentrations. As an aside, it may be noted that this accounts, at least in part, for the brownish color of smog. The gas can even become almost black in high concentrations at elevated temperatures. At room temperature (21°C) the gas is a mixture of the monomeric  $\text{NO}_2$  and the dimeric  $\text{N}_2\text{O}_4$  in equilibrium. About 16% is in form of  $\text{NO}_2$ . At 100°C this fraction has increased to 90% and at about 120°C practically all molecules are in the monomeric state. Only the monomeric  $\text{NO}_2$  absorbs visible light above 400 nm so gas temperature is an important parameter unless the isobestic point at about 350 nm, where both types have similar absorption, can be used. The absorption band is broad and almost continuous between about 300 nm and 600 nm with a region of high absorption without disturbance from  $\text{N}_2\text{O}_4$  approximately between 390 nm and 450 nm. The absorption can be measured using either a mercury source with emission lines either at 405 nm or 436 nm or a tungsten lamp filtered to give a wavelength band at the blue end of the spectrum. The problem with these measuring systems is that the source is slow which means that it is not possible to utilize the benefits of a system with high frequency modulation. Therefore, these systems, in addition to being quite bulky, power consuming, and complicated, are not suitable for fast measurements of very low concentrations (<1ppm) of nitrogen dioxide. In addition, at least the mercury source has limited lifetime.

In U.S. Patent 4,857,735, a spectrophotometer incorporating at least one light emitting diode is presented for conventional measurement of solutions. The absorption is measured through a short cuvette and the reference signal is obtained from measurement of a blank solution. This means that the measurement, in practice, is slow. A high light intensity is

essential for measuring solutions with sometimes very high absorbances. Therefore high current pulsing with a small duty cycle is important.

However, for gas measurements there is no need for such intensive pulses because the absorption is always small. The high current would produce excessive current noise which would badly disturb the gas measurement and raise the minimum level of detectable gas concentration. Because of the slow measurement, no means for correction of fast drifts are provided and because of the nature of the measurement no means for compensating changes in source intensity or detector sensitivity are present. The instrument as such would consequently not be suitable for measuring gases such as nitrogen dioxide.

#### BRIEF SUMMARY OF THE INVENTION

An object of the present invention is to provide a sensor assembly and method for the analysis of nitrogen dioxide with a radiation source efficiently emitting light in the blue end of the visible spectrum. A second object of the invention is to provide a sensor assembly, the source of which is modulatable at a frequency that is high compared to changes measurable e.g. in breathing gas. A third object of the invention is the provision of such a sensor assembly, which is both cheap and simple to construct and long-lasting and thus reliable for monitoring of toxic levels of nitrogen dioxide. A fourth object of the invention is to provide such a sensor assembly, which can measure small concentrations of nitrogen dioxide without interference from other gases, especially nitric oxide. A fifth object of the invention is the provision of such a sensor assembly, which in combination with a sensor for nitric oxide, can measure small concentrations of both nitrogen dioxide and nitric oxide in real time. A sixth object of this invention is to provide such a sensor assembly, which in combination with a gas converter, can also indirectly measure nitric oxide.

A salient feature of the sensor assembly according to the invention is that it can be made small, simple, fast, long-lasting, and reliable. The reason for this is that a light radiating diode is used as light source in the sensor assembly. Blue emitting light emitting diodes, commonly known as LEDs, with high enough optical power and long enough lifetime have not been

possible to produce commercially until recently. The emission spectrum of such a light emitting diode fits well to the absorption spectrum of nitrogen dioxide which means that all the benefits of light emitting diodes can be utilized. Since the only gas the sensor assembly reacts to is nitrogen dioxide and since the sensor assembly does not change the composition of the measured gas it is possible to make fast measurements of small concentrations of both nitrogen dioxide and nitric oxide by combining the sensor assembly with a sensitive and fast sensor for nitric oxide, preferably a sensor based on chemiluminescence.

Various other features, objects, and advantages of the invention will be apparent from the following detailed description and the drawings.

#### BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWING

The invention will be further understood by reference to the following detailed description taken in conjunction with the drawing, in which:

Figure 1 shows a spectrum of nitrogen dioxide in the visible and near-infrared region together with a typical emission spectrum of a light emitting diode suitable for use in the present invention;

Figure 2 shows, in longitudinal section, a sensor assembly for nitrogen dioxide according to the invention;

Figure 3 shows an alternative embodiment of a sensor assembly for nitrogen dioxide according to the invention;

Figure 4 shows an alternative sensor assembly for nitrogen dioxide according to the invention connected to an infrared sensor and a sensor for nitric oxide;

Figure 5 shows a system with an alternative sensor assembly according to the invention connected to be able to indirectly measure nitric oxide; and

Figures 6 and 7 show further embodiments of the sensor assembly according to the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

As previously mentioned, nitrogen dioxide ( $\text{NO}_2$ ) is one of the few gases that absorbs visible light. The absorption is caused by the complex electronic absorption system  $A^2B_1-X^2A_1$  with superimposed rotational fine structure. The maximum absorption is approximately at 390 nm, as can be seen in Figure 1, but the

absorption region is broad extending to about 600 nm and even further as a weak absorption. The red end of the spectrum will get more prominent with higher concentration and temperature. For low concentrations only the blue region below about 520 nm shows strong enough absorption to give a reliable measuring result. The concentration of nitrogen dioxide in Figure 1 was in the range of thousand ppm and the measuring length 100 mm. The absorption of nitrogen dioxide has earlier been used for measuring its concentration mainly for laboratory use. As radiation source a mercury lamp is typically used in order to get enough radiant energy in the blue region. Alternatively, a so called UV-VIS spectrophotometer could be applied to measure the absorption spectrum. For environmental purposes a laser or xenon lamp may be used to spectrally scan long paths of small concentrations of nitrogen dioxide in the air, a method called DOAS (Differential Optical Absorption Spectroscopy). The instruments are typically all slow, bulky, expensive, power consuming and not very sensitive for short measuring distances.

The development of light emitting diodes (LED) has been rapid during the last few years. Until recently it was not possible to manufacture light emitting diodes emitting in the blue region with good enough yield, high enough intensity, and long enough life time. Such a component is now e.g. manufactured by Nichia Chemical Industries Ltd. Of Anan, Japan. The emission spectrum of this LED is also shown in Figure 1 and it can be seen that the spectral features fit those of nitrogen dioxide absorbance very well. Moreover it is possible to take advantage of several features related to the LED when constructing a gas sensor. The LED is a very fast component meaning that high sampling rates can be used. In this way low frequency noise, so called 1/f noise, can be avoided without slowing down the response time. The LED is a very cheap component and it has a very low power consumption with low voltage as opposed to a mercury lamp. It is small size being a semiconductor chip. Thus it is possible to manufacture a small, cheap and sensitive NO<sub>2</sub> sensor with properties surpassing those of earlier measuring devices in many respects.

The preferred radiation source in this invention is a light emitting diode. However, another possible light radiating

diode to which considerable development efforts are being devoted is the laser diode. This component resembles a light emitting diode but is equipped with a resonator making laser action possible at currents higher than normally needed for good light output from a light emitting diode. The laser diode within the blue region is still expensive and not very reliable but in the near future the situation will change. The laser light emission from such a laser diode has a very narrow spectral bandwidth compared to the light emission from a light emitting diode. To a slight extent the spectrum of the light emitting diode as shown in Figure 1 will, however, also be present in the laser diode spectrum and could be used in a manner similar to what is described below for the light emitting diode.

A construction of the sensor assembly is shown in Figure 2. The radiation source 1 is a light emitting diode emitting in the blue region with maximum radiation between about 380 nm and 520 nm depending on the construction of the diode. The specific LED, the emission spectrum of which is shown in Figure 1, has its emission maximum at about 450 nm. The LED chip 1 in Figure 2 is shown in a typical LED case with a reflector and a plastic lens that collimates the radiation. Of course it could be different but the standard package is beneficial because it is efficient and cheap. It could also be replaced by a laser diode.

The gas to be measured is normally confined to a sample chamber 2 which typically is a long tube with two end windows 3a and 3b, reflecting inner walls 4 and gas inlet 5a and outlet 5b. The length of this chamber could be about 100 mm for rapid measurements of a sampled gas. If the intention is to measure e.g. breathing gas, a response time of about 200 ms is required in order to resolve all details of the inspiration and expiration. Of course, the sample chamber could also look different, e.g. be folded using mirrors, or it could even be absent for environmental measurements. For a fast sampling measurement, the sample chamber 2 in Figure 2 is, however, the simplest. A sample chamber is needed especially if the sample gas is to be measured at a higher temperature than ambient or temperature stabilization is applied. The benefit of a higher measuring temperature is not only to prevent condensation of water on the windows 3 but to get more signal. As pointed out



above, more nitrogen dioxide is formed by conversion from the dimeric form  $N_2O_4$  as temperature rises until all the oxide is in the monomeric form  $NO_2$  at about  $120^\circ C$ . The dimeric form does not absorb in the visible region which means that at higher temperature a deeper absorption and subsequently a better signal and higher sensitivity will result. It is not necessary to heat the sampled gas to  $120^\circ C$ . If heating is applied with a heating element 6 a temperature around  $50^\circ C$  seems adequate for practical reasons. For less sensitive measurements, where the danger of water condensation is absent, heating can be omitted. However, the temperature of the sampled gas must be measured in order to compensate the measured concentration value. In Figure 2 this is done using temperature sensor 7, which preferably could be a thermistor or some other semiconductor component. The foregoing temperature dependence can be stored in memory in a control unit and used for compensation of the total nitrogen dioxide gas concentration according to the measured gas temperature. Other temperature dependencies in the assembly, for example, that of the radiation source and/or that of the detector, may be similarly stored to so as to provide a single temperature dependence function or table for use in the sensor assembly.

The radiation from an LED 1 of the type described above is quite well collimated. Part of the radiation, 8a goes straight through the sample chamber and the rest, 8b, is reflected off the inner wall 4. The radiation is, in other words, efficiently transmitted through the sample chamber to a detector 9. Even if the LED is preferable because of cost reasons, the radiation transfer would be even simpler using a laser diode because of its beam coherence and the subsequent possibility to collimate the beam very accurately. The detector 9 can preferably be a conventional silicon detector or a so called blue enhanced type of detector, such as that made and sold by United Detector Technology of Hawthorne, CA. Such a component is fast enough to resolve even a high sampling frequency. A sampling frequency of at least about 10 Hz is required for resolving a breathing curve but in this case it is beneficial to work in the kHz range or even higher to avoid  $1/f$  noise. The detector can be connected to a control unit having a narrowband amplifier centered at this high sampling frequency with good

signal-to-noise ratio and good stability as a consequence. An optical filter 10 is positioned in front of the detector 9 to prevent ambient light from disturbing the measurement. Of course the sensor assembly should in practice be built into a light tight case. The filter can be a blue color filter or it can be a narrow band Fabry-Perot filter centered at or near the maximum of the spectral radiation of the LED or laser diode. An accurate measurement is also sensitive to changes in the zero signal, i.e. the signal without absorbing gas. Slow changes can be compensated for by occasionally filling the sample chamber with gas free from NO<sub>2</sub> and measuring and storing this signal for use as a denominator when calculating the gas transmission. This principle does not work for fast changes or in cases when it is not possible to fill the space between the LED source 1 and the detector 9 with non-absorbing gas. There are a number of conventional ways to compensate for such fast changes. If the main source of changes is the LED itself it may be sufficient to monitor its light output using an optical reference detector 11 near the LED as shown in Figure 1. The LED of source 1 is normally connected to a constant current source with a modulation option and the detector 11 can be wired to give feedback to this power source to achieve additional optical stabilization. The so called dark signal is registered when the LED source 1 is in its off state and no light is reaching the detector 9. When both the dark level and zero level are known, the real gas absorption can be calculated and the gas concentration found after linearization and calibration of the sensor assembly. A logarithmic linearization curve is almost correct in this case because Lambert-Beer's law is obeyed as opposed to most infrared gas absorption measurements. However, this fact is of minor importance today when microcomputers can handle any measured linearization function.

It may not be enough to monitor only changes in the LED as shown in Figure 2 or only slow changes in the zero signal. Dirt can accumulate on the windows 3 and walls 4 of sample chamber 2. To compensate for such changes, a reference detector 11 may be provided at the other end of the sample chamber 2 as shown in Figure 3. A beam splitter 12 reflects part of the radiation 8a and 8b on the reference detector 11. An optical

filter 13 in front of the detector 11 has the same function as filter 10. However, the wavelength region seen by detector 9 and reference detector 11 must be different so that the signal from reference detector 11 is not sensitive, or is least less sensitive, to the light absorption in nitrogen dioxide. As it is beneficial to use the same source 1 for both detectors, the wavelength region has to be divided. The long wavelength part of the LED emission, in Figure 1 above about 480 nm, could be used for detection by reference detector 11. To achieve this, either beam splitter 12 can be dichroic with an edge at about 480 nm, or filter 13 can be transmissive for wavelengths above the limit if the beam splitter is conventional. There is still gas absorption in that region but to a smaller extent than at the maximum of the LED emission. In other words, the ratio between the measured signal and the reference signal will react to the absorption of nitrogen dioxide. It is also possible to use the small emission in the near-infrared region about 950 nm shown in Figure 1 as reference. Also here a slight gas absorption is observed. However, the occurrence and strength of this emission depends on the LED manufacturing process and furthermore this wavelength region does not necessarily reflect the intensity changes at the blue end of the spectrum because of different absorption properties of the possible dirt and a fairly strong wavelength dependence of light scattering.

In Figure 4 another embodiment of the sensor assembly in Figure 3 is shown. Here no beam splitter is used and detector 9 with filter 10 and reference detector 11 with filter 13 are both positioned side-by-side and optically shielded from each other. This figure also shows a measuring system for fast measurement of other gases. A measuring system 14 for infrared absorption is connected in series with the NO<sub>2</sub> sensor assembly 29. In this way it is possible to measure e.g. carbon dioxide. The sampled gas 15 is drawn into the system using a pump 16. Normally it is not important which sensor is connected nearer to the sampled gas inlet 15 but sometimes, especially in connection with breathing gases, it is necessary to have a fastest possible carbon dioxide signal and this necessitates a position of the corresponding sensor near the sampled gas inlet 15. In the gas stream it is often necessary to have a gas drying system 17 to

avoid water condensation and infrared absorption. A simple solution is to connect a Nafion tube in the sampling line. For establishing a zero level a valve 18 can be turned to an inlet of reference gas 19, normally ambient air, with possible scrubber 20 to remove nitrogen dioxide and other disturbing gases, e.g. carbon dioxide CO<sub>2</sub> and nitric dioxide NO.

Downstream and after the nitrogen dioxide sensor assembly 29 it is possible to connect a sensor 21 for nitric oxide (NO). It can be a conventional electrochemical cell but if small concentrations are to be measured with fast response a chemiluminescent sensor is a better choice. Such instruments are e.g. manufactured by Sievers Instruments, Inc. of Boulder, Colorado as product Model 280. These sensors normally consist of a gas flow restricting element 22 to create underpressure in a reaction chamber 23, an ozone generator 24 with its flow restricting element 25 and a sensitive detector 26, normally a photomultiplier tube. The ozone supplied to the chamber 26 reacts with possible nitric oxide in the sampled gas to form nitrogen dioxide in an excited state and the relaxation creates photons that are detected by detector 26 and are related to the concentration of nitric oxide. Since nitrogen dioxide is formed in sensor 21, this sensor has to be downstream from other sensors. Additionally, the ozone component contaminates and dilutes the sample. A scrubber 27 is normally connected in the sampling line after the nitric oxide sensor to remove ozone and other toxic gases before they are pumped out to the outlet 28 of the system.

In principle also small concentrations of nitrogen dioxide can be measured using the chemiluminescent sensor 21 if the NO<sub>2</sub> content is first converted to NO by heating. This is the conventional way to measure NO<sub>2</sub> but simultaneous fast measurements of both NO<sub>2</sub> and NO are not possible to perform. First, the NO content must be measured, then the sum of the NO<sub>2</sub> to be measured and converted to NO is measured, and the actual NO<sub>2</sub> concentration is obtained by subtraction. Such a measurement is very vulnerable and apt to changes in e.g. the NO concentration. The measurement is in other words not suitable for real time measurement of e.g. breathing gases. The nitrogen dioxide sensor assembly 29, on the contrary, does not alter the

measured gas in any way and a possible content of nitric oxide remains intact so that also it can be measured directly using sensor 21.

In Figure 5 another alternative construction of the nitrogen dioxide sensor assembly is shown. Only one detector 9 is needed because a revolving filter wheel 32 has been used to alternately position filter 10 and filter 13 in front of the detector 9. In this way any differences in characteristics that would arise when two detectors are used are eliminated.

Naturally, the revolving speed of filter wheel 32 must be kept lower than the modulation frequency of the LED.

The system shown in Figure 5 shows like Figure 4 another possibility for connecting the nitrogen dioxide sensor assembly 29. In addition to being a cheap and reliable sensor for monitoring toxic levels of nitrogen dioxide, according to Figure 5, it is even possible to indirectly measure nitric oxide with sensor 29 by first converting the NO content into NO<sub>2</sub> in a gas mixer 30 e.g. by letting it mix and react with ozone or oxygen 31. For slow measurements the oxygen in air is adequate for this purpose but for fast measurements ozone can be used. The embodiment of Figure 5 thus becomes a very cheap and simple way to monitor, especially, relatively high concentrations of NO (normally ppm level to a level of a few decades of ppm) e.g. in a gas container. The NO<sub>2</sub> content, if any, in the sample gas 15 can be measured at first and then the NO content can be found out by subtracting this NO<sub>2</sub> content from the total amount of NO<sub>2</sub>, including the converted NO amount, compensated for the added gas flow 31 from the gas mixer 30. The difference is the NO content.

Another possibility would be to use the chemiluminescent NO sensor 21 as the mixer and NO converter instead of mixer 30 shown in Figure 5 and connect it in front of the NO<sub>2</sub> sensor assembly 29. In this way the NO sensor 21 would first measure the NO content in the sampled gas, then rapidly convert it into NO<sub>2</sub>, which would be measured by the NO<sub>2</sub> sensor assembly 29, and the actual NO<sub>2</sub> content would be found as the difference between this total NO<sub>2</sub> content, compensated for the added ozone gas flow and the NO<sub>2</sub> content resulting from NO conversion. However the configuration shown in Figure 4 gives a more direct measurement and it is therefore deemed more reliable

and preferable than the configuration shown in Figure 5.

Figures 6 and 7 present alternative embodiments of the sensor assembly with only one source 1 and one detector 9. Both have a reflecting chopper wheel 33 with a hole in it so that the radiation either goes straight through the sample chamber 2 or is reflected into an alternative reference path on its way to filter 10 and detector 9. In Figure 6 the reference path consists of an optical fiber 34 which transfers the radiation to detector 9. Then it is possible to compensate both for fluctuations in the source radiation and changes in detector sensitivity.

If, in addition, it is necessary to compensate for possible disturbing absorption in the sample gas flow or chamber, a reference chamber 36 can be connected to the sample flow in such a way that any NO<sub>2</sub> content of the sample gas at inlet 15 is removed using a scrubber 38 shown in Figure 7. It would also be possible to connect reference chamber 36 to some other usable gas flow or even use it without gas flow, especially if it could be expected that both chambers 2 and 36 behave similarly when it comes to disturbing absorption. The radiation is directed through reference chamber 36 via mirrors 35 and 37 and using a beam splitter 12. Of course, other optical arrangements are also possible.

Even though many different possibilities have been shown how to use a fast and simple nitrogen dioxide sensor assembly based on a light radiating diode it is evident that many variations of the sensor assembly and many other applications within this invention are possible to construct.

It is recognized that other equivalents, alternatives, and modifications aside from those expressly stated, are possible and within the scope of the appended claims.

## CLAIMS

1. A sensor assembly for use in the optical absorption analysis of NO<sub>2</sub> content of a gas sample, said sensor assembly comprising:

5 a semiconductor radiation source emitting radiation having a emission spectrum with a maximum wavelength of about 600 nm;

a sample chamber for containing the gas sample, the NO<sub>2</sub> content of which is to be measured, the radiation from said radiation source passing through said sample chamber; and

10 a detector for receiving the radiation passed through the gas sample in said sample chamber and for providing an output signal indicative of the NO<sub>2</sub> content of the gas sample in said sample chamber.

2. A sensor assembly according to claim 1 wherein said semiconductor radiation source is further defined as emitting radiation having an emission spectrum with a maximum wavelength of about 520 nm.

3. A sensor assembly according to claim 1 wherein said semiconductor radiation source emits radiation in an emission spectrum between about 380 - 520 nm.

4. A sensor assembly according to claim 1 wherein said semiconductor radiation source comprises a light emitting diode.

5. A sensor assembly according to claim 1 wherein said semiconductor radiation source comprises a laser diode.

6. A sensor assembly according to claim 1 further including a further detector for detecting the emitted radiation of said radiation source, said further detector being connected to a power supply for said radiation source for stabilizing the  
5 operation of said radiation source.

7. A sensor assembly according to claim 1 wherein said detector comprises a silicon detector.

8. A sensor assembly according to claim 1 wherein said detector comprises a blue enhanced type of detector.

9. A sensor assembly according to claim 1 wherein said detector is coupled to an output signal amplifier.

10. A sensor assembly according to claim 9 wherein said radiation source is operated at a sampling frequency and wherein said output signal amplifier is a narrow bandwidth amplifier, the bandwidth of which is centered at said sampling frequency.

11. A sensor assembly according to claim 1 further including an optical filter interposed in front of said detector along a path of the emitted radiation in said sensor.

12. A sensor assembly according to claim 11 wherein said optical filter passes a spectral band centered on a maximum of the emission spectrum of said radiation source.

13. A sensor assembly according to claim 1 further including a reference detector for detecting the radiation passed through the gas sample in said sample chamber and for compensating said first mentioned detector.

14. A sensor assembly according to claim 13 wherein said reference detector includes means for reducing the sensitivity of said reference detector to spectral absorption resulting from the presence of NO<sub>2</sub> in the gas sample.

15. A sensor assembly according to claim 14 wherein said reducing means comprises means for causing a different spectral region of said emission spectrum to be applied to said reference detector than the spectral region of said emission spectrum applied to said first mentioned detector.

16. A sensor assembly according to claim 15 wherein said means applying different spectral regions of said emission spectrum to said first mentioned detector and said to reference



detector comprises a dichroic beam splitter interposed in a path  
5 of the radiation exiting said sample chamber for applying beams  
of different spectral regions to said first mentioned detector  
and said reference detector.

17. A sensor assembly according to claim 15 wherein  
said means applying different spectral regions of said emission  
spectrum to said first mentioned detector and to said reference  
detector comprises filters interposed in front of said first  
5 mentioned detector and said reference detector, said filters  
passing different spectral regions of said emission spectrum to  
said first mentioned detector and said reference detector.

18. A sensor assembly according to claim 13 wherein  
said radiation source emits radiation in a further emission  
spectrum and wherein said reference detector detects radiation in  
said further emission spectrum.

19. A sensor assembly according to claim 1 further  
including means having a pair of filters, said filters passing  
different spectral regions of said emission spectrum and means  
for placing one or the other of said filters in front of said  
5 detector along a path of the radiation in said sensor for  
providing compensation to said detector.

20. A sensor assembly according to claim 1 further  
including a temperature sensor for sensing the temperature of the  
gas sample in said sampling chamber and means for compensating  
the output signal of said detector in accordance with the sensed  
5 temperature of the gas sample.

21. A sensor assembly according to claim 20 wherein  
said sample chamber has a heater operatively associated  
therewith.

22. A sensor assembly according to claim 1 further  
including inlet and outlet conduits coupled to said sample  
chamber for providing gas flow through said sample chamber, and

wherein an additional gas sensor is located in one of said  
5 conduits.

23. A sensor assembly according to claim 22 wherein said additional gas sensor comprises an infrared absorption sensor.

24. A sensor assembly according to claim 23 wherein said infrared absorption sensor is located in said inlet conduit.

25. A sensor assembly according to claim 22 wherein said additional gas sensor comprises a NO sensor.

26. A sensor assembly according to claim 25 wherein said NO sensor is located in said outlet conduit.

27. A sensor assembly according to claim 25 wherein said NO sensor is further defined as one capable of measuring NO<sub>2</sub>.

28. A sensor assembly according to claim 1 further defined as one for additionally measuring the NO content of the gas sample, and further including an inlet conduit providing a gas sample to said sample chamber and wherein said inlet conduit  
5 includes a reactor for converting NO in the gas to NO<sub>2</sub>, and wherein said detector includes means for determining the NO content of the gas from sequential measurements of the NO<sub>2</sub> content of gas samples in said sample chamber.

29. A sensor assembly according to claim 1 further defined as one for additionally measuring the NO content of the gas sample, and further including an inlet conduit for providing a gas sample to said sample chamber and wherein said inlet  
5 conduit includes a reactor, said reactor includes means for measuring the NO content of said gas sample, said reactor thereafter converting NO in the gas sample to NO<sub>2</sub>, said detector including means for determining the NO<sub>2</sub> content of the gas sample from sequential measurement of the NO<sub>2</sub> content of gas samples in  
10 said sample chamber.

30. A method for determining the NO<sub>2</sub> content of a gas sample comprising the steps of:

providing a gas sample;

5 passing radiation from a semiconductor radiation source through the gas sample, said radiation having an emission spectrum with a maximum wavelength of about 600 nm; and

10 sensing the radiation exiting the gas sample for determining the NO<sub>2</sub> content of the gas sample from the optical spectral absorption characteristics of the sensed radiation resulting from the presence and amount of NO<sub>2</sub> in the gas sample.

31. The method according to claim 30 further defined as passing radiation having an emission spectrum with a maximum wavelength of about 520 nm.

32. The method according to claim 30 further defined as passing radiation having an emission spectrum with wavelengths in a range of about 380 - 520 nm.

33. The method according to claim 30 further defined as passing radiation from a light emitting diode radiation source through the gas sample.

34. The method according to claim 30 further defined as passing radiation from a laser diode through the gas sample.

35. The method according to claim 30 further including the step of carrying out a further sensing of the radiation exiting the gas sample and using the results of said further sensing to provide compensation to said first mentioned sensing.

36. The method according to claim 35 wherein said further sensing is carried out under conditions of reduced sensitivity to spectral absorption resulting from the presence of NO<sub>2</sub> in the gas sample.

37. The method according to claim 36 wherein said further sensing is carried out using a different spectral region

of the emission spectrum than is employed in said first mentioned sensing.

38. The method according to claim 36 wherein said further sensing is carried out using a different emission spectrum than is used in said first mentioned sensing.

39. The method according to claim 30 further defined as sensing the temperature of the gas sample and compensating the sensing results of said sensing step.

40. The method according to claim 39 further defined as heating the gas sample.

41. The method according to claim 30 further including the step of carrying out an additional gas sensing procedure on the gas sample.

42. The method according to claim 41 wherein the further gas sensing procedure is further defined as employing infrared absorption.

43. The method according to claim 41 wherein the further gas sensing procedure senses NO.

44. The method according to claim 43 wherein the further gas sensing procedure includes the step of converting NO in the gas sample to NO<sub>2</sub>, and wherein the sensing step is further defined as determining the NO content of the gas sample from sequential measurements of the NO<sub>2</sub> content of gas samples.

45. The method according to claim 41 wherein the further gas sensing procedure measures NO content of the gas sample and converts NO in the gas sample to NO<sub>2</sub>, and wherein said sensing step is further defined as determining the NO<sub>2</sub> content of the gas sample from sequential measurements of the NO<sub>2</sub> content of gas samples.

1/3

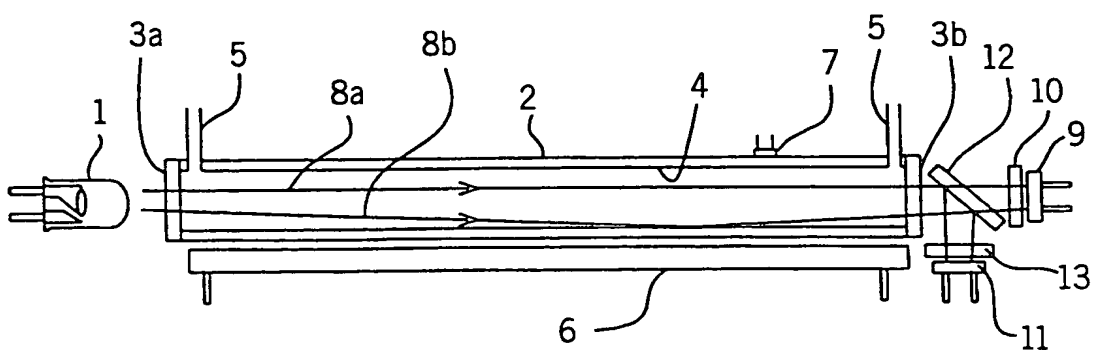
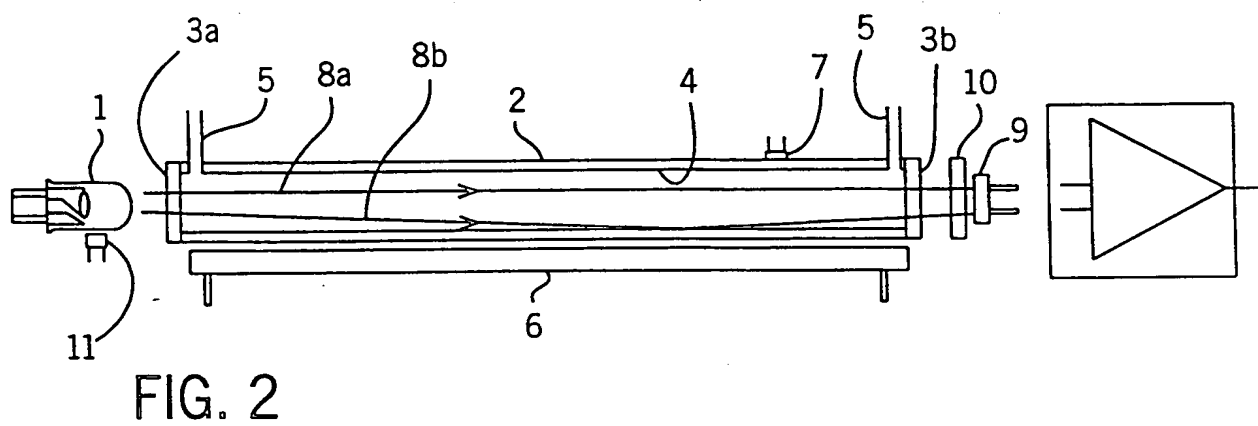
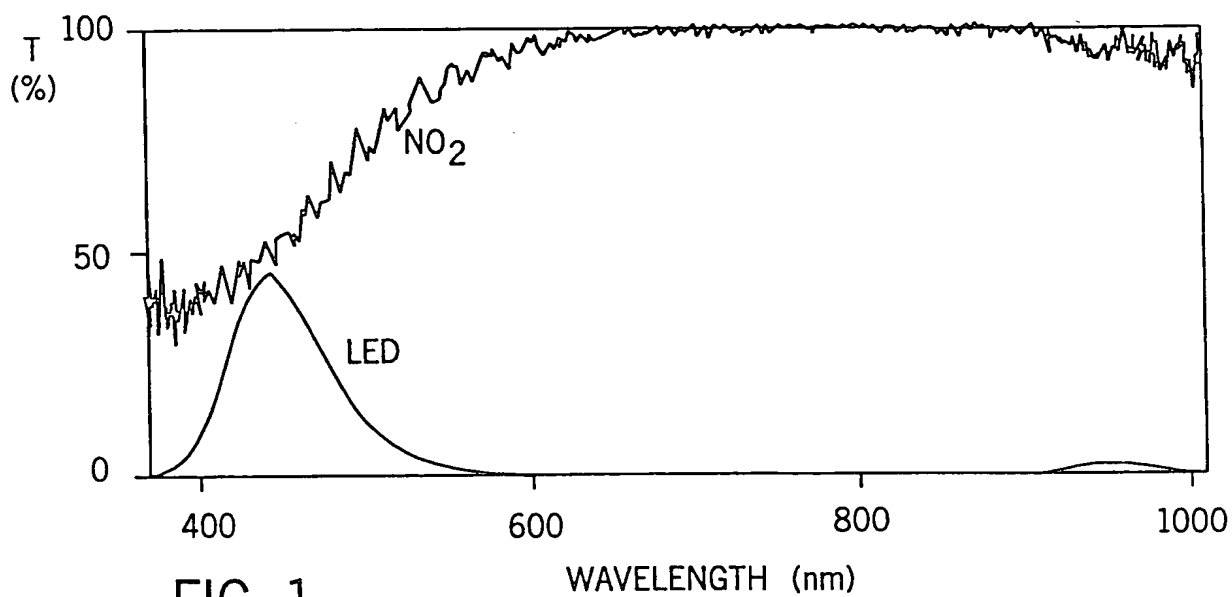


FIG. 3

2 / 3

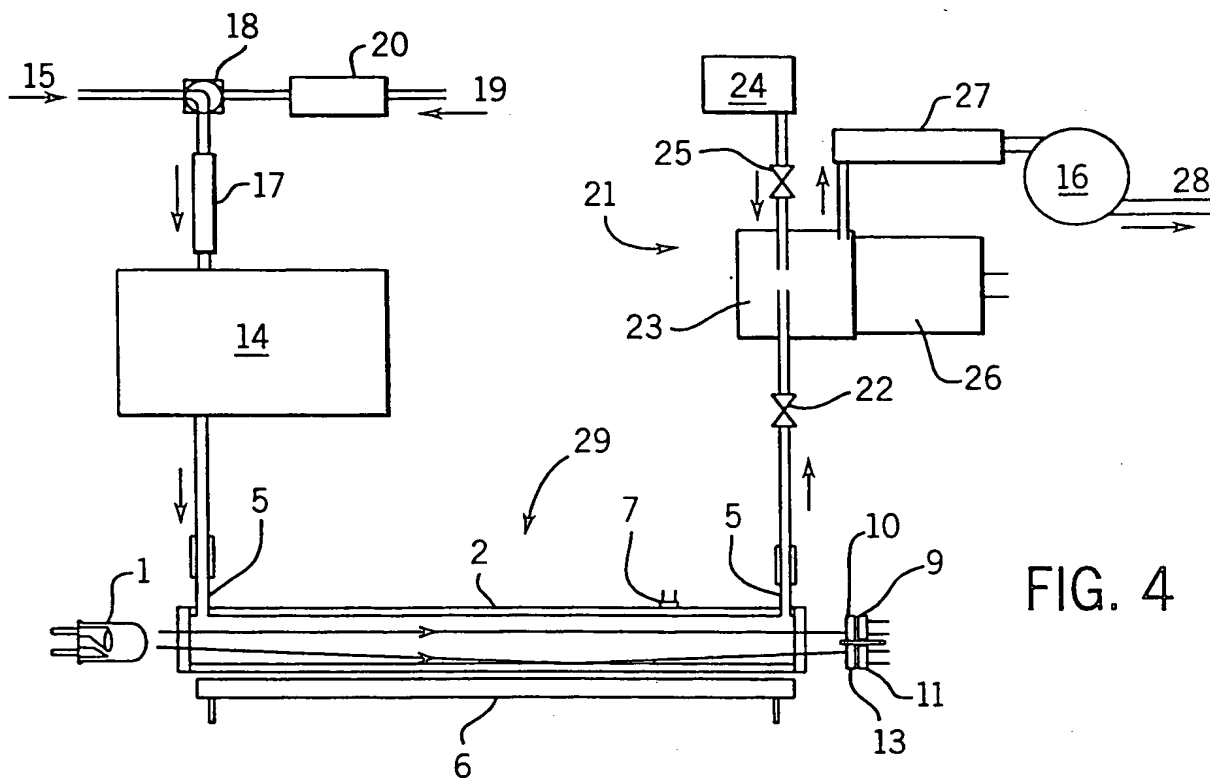


FIG. 4

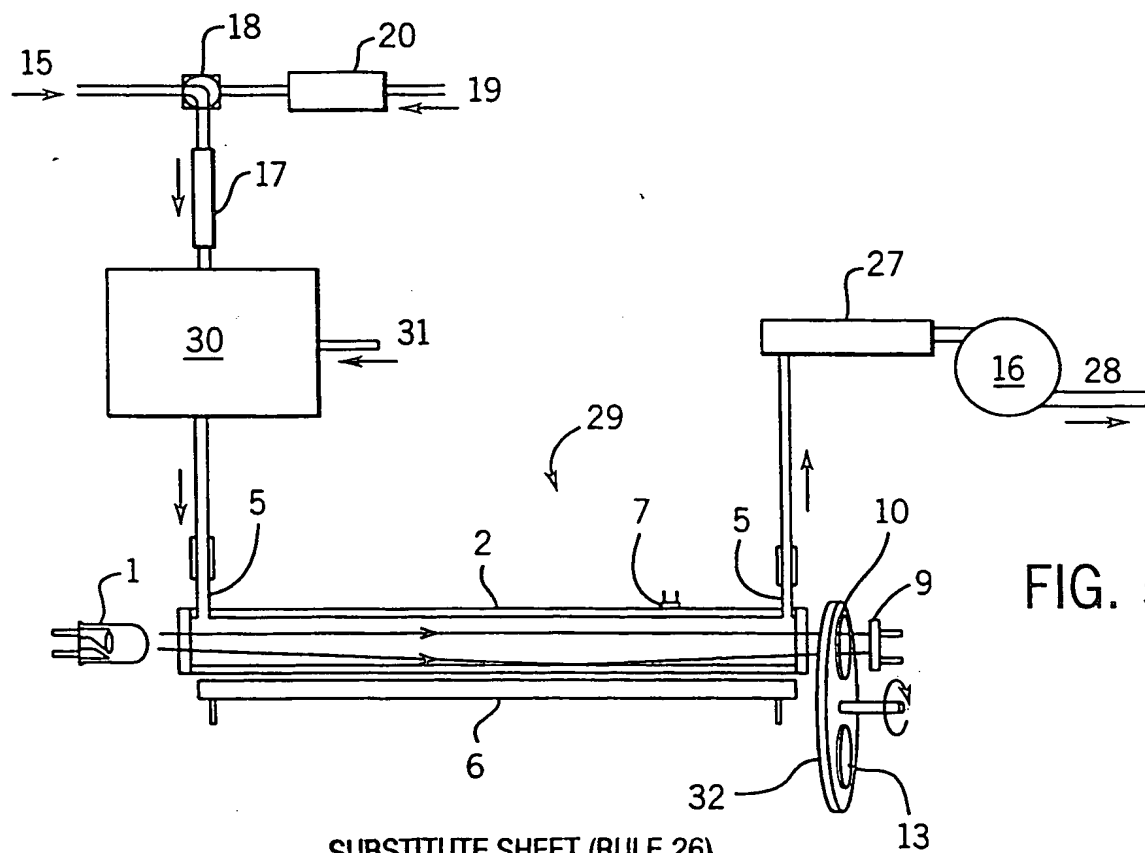
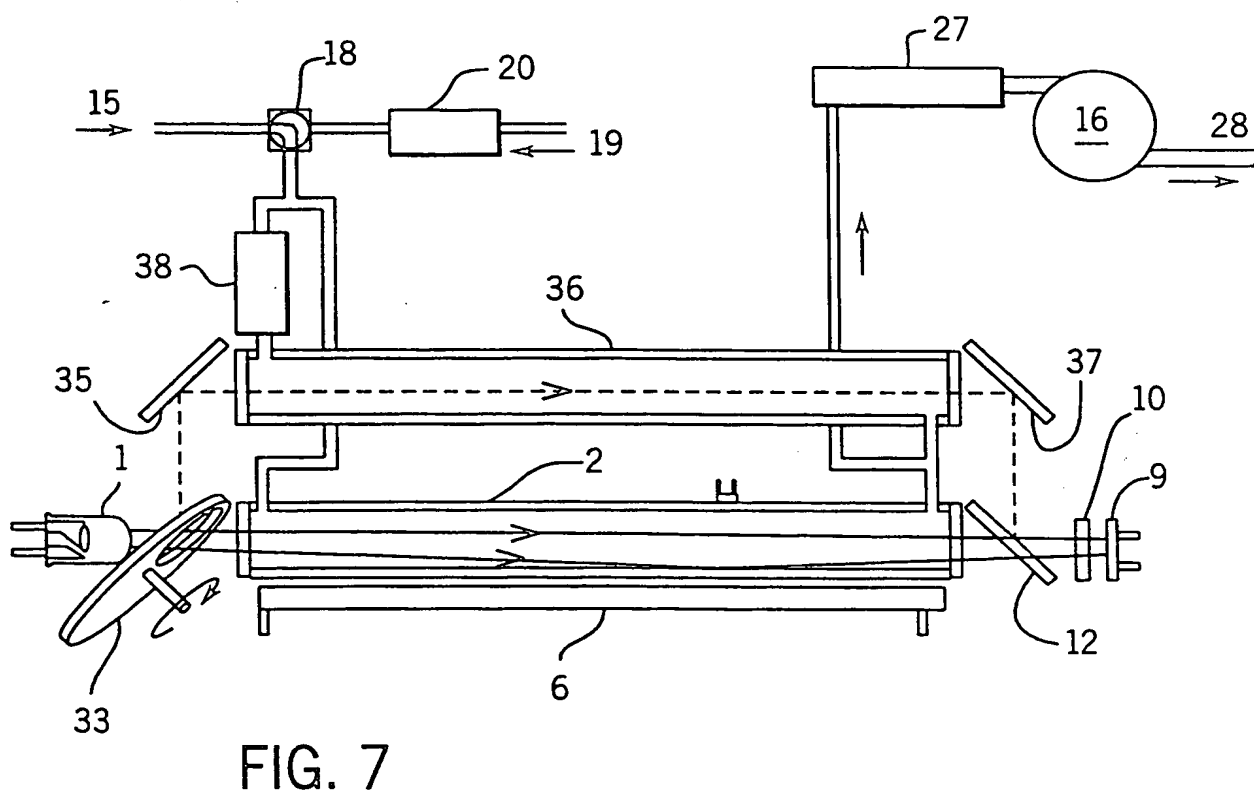
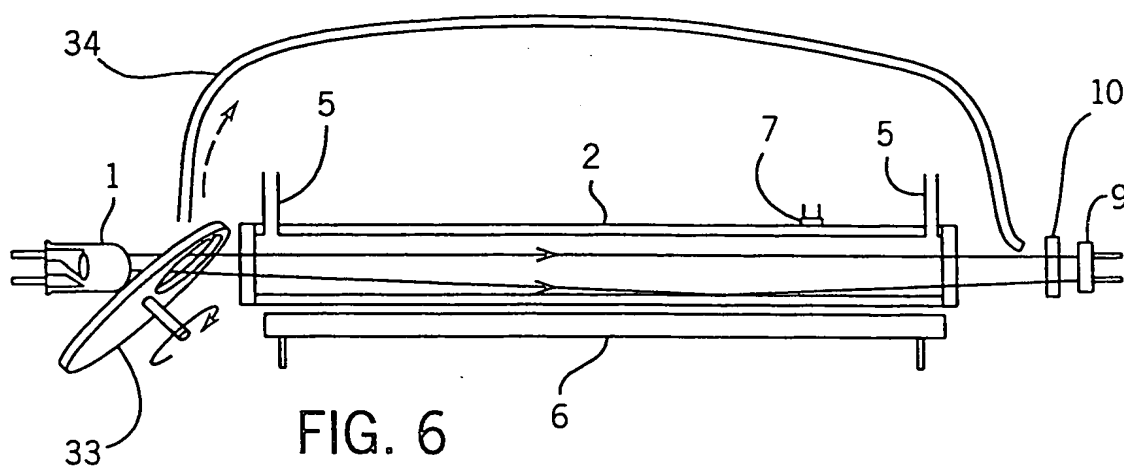


FIG. 5

3 / 3



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 99/00645

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 G01N21/31 G01J3/10

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 G01N G01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 2 303 447 A (AMG SYSTEMS LIMITED) 19 February 1997  see page P2, line 8 - line 34 see page 5, line 14 - line 16 see page 3, line 17 - line 28 see page 11; figures 1,5	1-5, 7-9, 11-17, 19, 30-37
A	DATABASE WPI Section Ch, Week 7913 Derwent Publications Ltd., London, GB; Class E36, AN 79-24361B XP002106208 -& JP 54 021896 A (MITSUBISHI HEAVY IND CO LTD), 19 February 1979 see abstract; figures 1,2  -/--	1-3, 8, 30-32

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

17 June 1999

Date of mailing of the international search report

25/06/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+31-70) 340-3016

Authorized officer

Scheu, M



# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 99/00645

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2303447 A	19-02-1997	NONE	
US 3718429 A	27-02-1973	CA 939926 A DE 2119939 A	15-01-1974 05-10-1972
US 4857735 A	15-08-1989	NONE	
US 5818598 A	06-10-1998	NONE	